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TITLE THE APPLICATION OF TIME-RESOLVED LUMINESCENCE SPECTROSCOPY TO A REMOTE URANYL SENSOR

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The application of time-resolved luminescence spectroscopy to a remote uranyl sensor

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ABSTRACT

Time resolved luminescence spectroscopy is an effective method for the determination of a wide range of uranyl concentrations in aqueous samples. We have applied this technique to the development of a remote sensing device using fiber optic cables coupled with a micro flow cell in order to probe for uranyl in aqueous samples. This sensor incorporates a Nafion membrane through which UO_2^{2+} can diffuse in to a reaction/analysis chamber which holds phosphoric acid, a reagent which enhances the uranyl luminescence intensity and lifetime. With this device, anionic and fluorescing organic interferences could be eliminated, allowing for the determination of uranyl over a concentration range of 10^{-4} to 10^{-9} M.

1. INTRODUCTION

Laser induced time resolved luminescence (LITRL) spectroscopy is an effective method for the determination of a wide range of UO_2^{2+} concentrations in aqueous samples.¹⁻³ This is because upon excitation, uranyl shows an intense green emission which is easily detected and quantified. We have taken advantage of this technique to create a sensor through which we can establish a remote and nearly real time analysis of uranyl concentration in aqueous solutions. In this sensor application the excitation beam is carried to the sample and the emitted radiation is carried to the photomultiplier using fiber optic cables which are connected to a flow cell. The use of chemical and physical sensors which apply fiber optic technology has increased tremendously in the past decade.⁴⁻⁶ However, there are only a few reports in which laser-based

time resolved luminescence measurements have been used with fiber optics in an analytical manner.^{7,8}

1.1 Sensor Design

Several different designs of the uranyl sensor were tested, the most successful being outlined in Fig. 1.

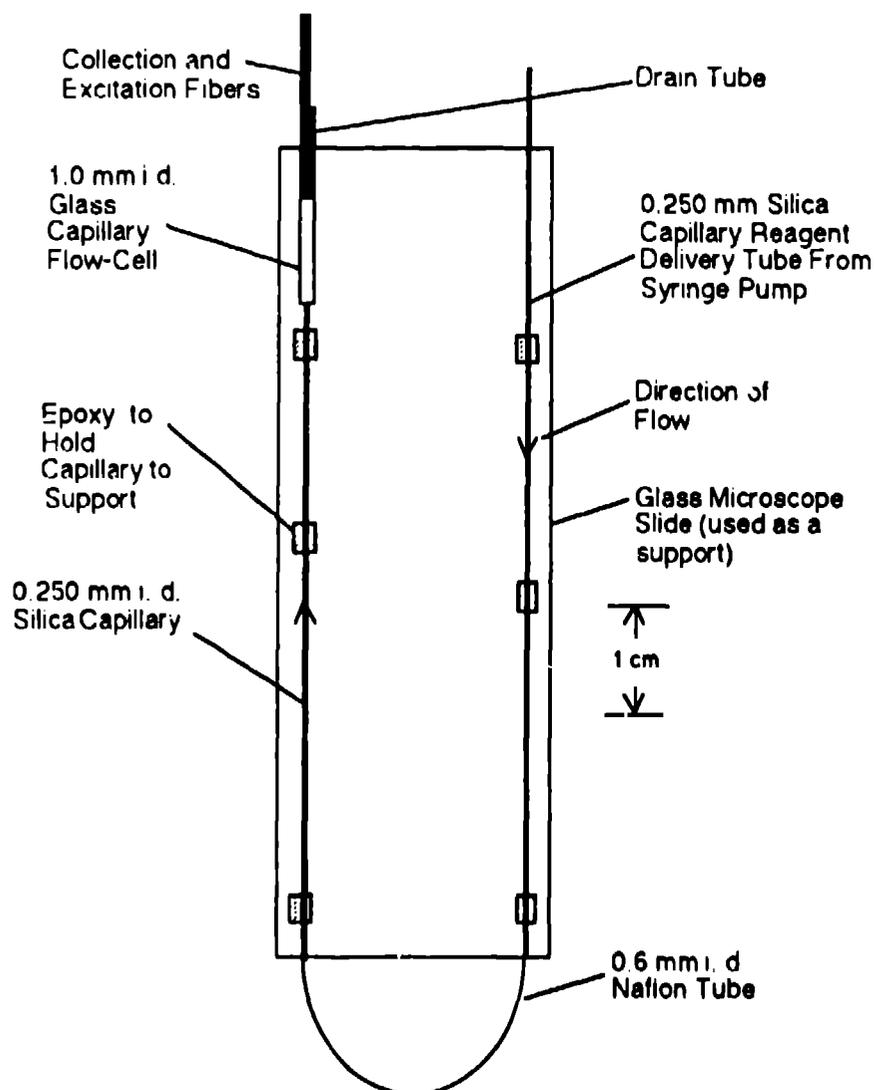


Figure 1 Diagram of the uranyl sensor

For this design, a 250 μm inner diameter silica microcapillary tube, purchased from Polymicro Inc., was sealed into the top of a Nafion tube (0.6 mm inner diameter) with UV-curable epoxy (Norland Products, Inc.)

Another short length of tubing is used to connect the bottom of the Nafion tube to a short piece of glass capillary tube (2 mm inner diameter) which acts as a micro-flow cell. Two 200 μm fibers and a microcapillary drain tube are sealed in the top of the glass capillary with epoxy. For this sensor, the flow reagent is phosphoric acid. This reagent enhances both the uranyl emission intensity and excited state lifetime ($\sim 200 \mu\text{s}$ at 295 K in 1 M H_3PO_4) compared to other aqueous acidic solvents, thereby leading to lower detection limits.^{2,9} This reagent is also used to flush the system and renew the chemistry in between readings. Using this experimental setup, it is possible to obtain a fairly rapid and accurate determination of uranyl concentration using a simple physical measurement.

2.2 Experimental Procedure and Set-up

Analysis is done in a stopped-flow manner. Reagent is pumped through the Nafion tube and flow-cell to regenerate the sensor. Flow is then stopped, and the sensor is allowed to equilibrate in an aqueous solution of analyte. During this time, uranyl ions can diffuse from the aqueous sample into the Nafion tube containing phosphoric acid. After a set equilibration time, typically 30 minutes, an appropriate amount of phosphoric acid is pumped through the system in order to extract the uranyl from the Nafion membrane and push the sample into the flow cell for spectroscopic analysis. The total void volume in the Nafion tube, the short capillary tube connecting the cell, and the microcell, is estimated to be 30 μl so very little flow reagent is used. After a measurement is taken, 200 μl of reagent is pumped through the system to renew the chemistry, and the process is repeated. An advantage of using this design is that the glass microcell is never immersed in solution. Therefore, any changes in the refractive index, absorption coefficient, or the presence of scattering agents in the solution does not affect the back scatter of light into the collection fiber. In addition changes in the optical properties of the Nafion tube do not affect the amount of light received in the collection fiber. The concentration range of uranyl that can be measured is 10^{-4} to 10^{-9} M. A schematic of the FFR apparatus incorporating the uranyl sensor is shown in Fig. 2.

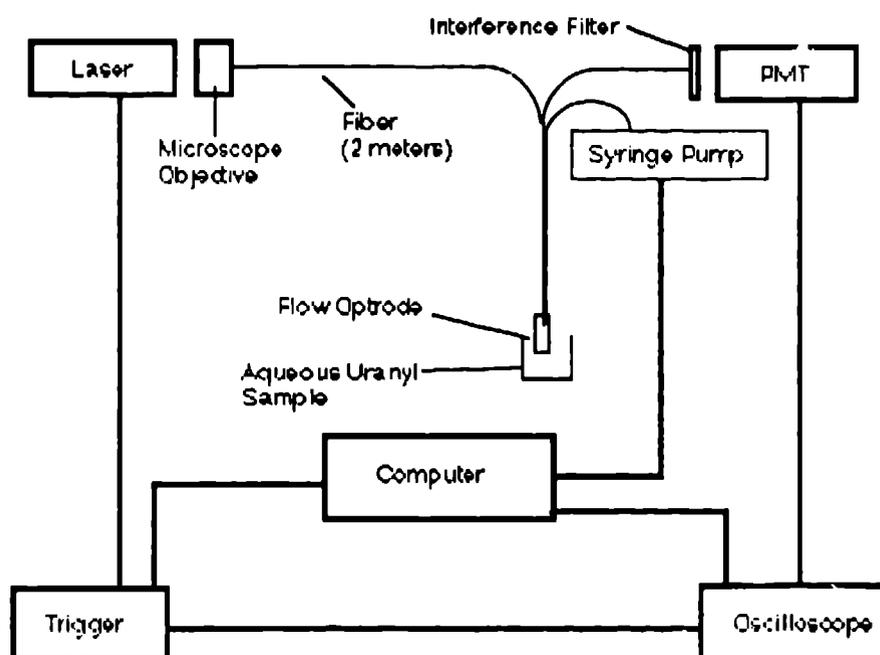


Fig 2 Experimental setup for the fiber optic based, time-resolved luminescence measurements.

In this setup, the excitation beam was provided by a LSI VSL337 Nitrogen laser which has an output of 150 $\mu\text{J}/\text{pulse}$ with a 3 ns pulse width at 337 nm. Fiber-optic cables which can transmit ultraviolet radiation were purchased from 3M. The laser beam was focused on to the fiber optic cable with a microscope objective. An interference filter was placed directly in front of the PMT housing to eliminate any stray light or laser scattering from entering it and so that only the emitted radiation from 480-520 nm (where the majority of the uranyl emission occurs) was collected. The output signal from the Hamamatsu R955 PMT was coupled to a LeCroy 9410 digital oscilloscope which was interfaced to an IBM PC for analysis purposes. To pump the phosphoric acid reagent into the uranyl sensor, a Hamilton Micro Lab 900 programmable syringe pump was used. Teflon fittings were used since H_3PO_4 leaches iron out of the metal fittings, leading to quenching of the uranyl emission.

2. Results and Discussion

In this paper, we report on the development of a sensor which couples the well established LITRL method for uranyl analysis with a preconcentration technique using a Nafion membrane separating a sample solution from a phosphoric acid medium. Nafion, shown below, is a durable permselective perfluorosulfonate ion exchange material which, when cast in the form of a membrane, can be used for the transport of cations from one aqueous solution to another. When dilute solutions are in contact with the Nafion, solution-phase anions cannot penetrate the membrane. The reason for this is Donnan exclusion which is due to the high concentration of fixed anionic sites within the membrane and the subsequent build up of a cationic double layer charge boundary around the membrane [10,11]. Thus, for our system, anions such as chloride are excluded from the phosphoric acid medium. This is a significant advantage for this study as halides are among the most likely uranyl quenchers to be found in groundwater. There have been several studies concerning the general structure and properties of Nafion as well as on the rate of ion diffusion through the membrane [11]. In addition to ion transport, osmotic flow of water will also occur.

2.1. Emission Lifetimes and Interferences

Uranyl ion was determined in H_3PO_4 over a concentration range of 10^{-4} to 10^{-2} M using LITRL fiber optic based measurements, and 10^{-3} to 10^{-6} M using steady state luminescence measurements. The steady state uranyl emission signal is swamped by the large fluorescent background at low concentrations. The primary advantage of time resolving the spectrum is the ability to discriminate against intense, short-lived (< 100 ns) fluorescence due to organics in solution and/or scattered radiation. This is possible since the UO_2^{2+} excited state lifetime is 200 μs in phosphoric acid. By analyzing the signal between 45 and 55 μs after the laser excitation pulse, we observed emission intensity due solely to the uranyl ion excited state. In addition, the measurement of excited state lifetimes makes it possible to monitor changes in environment that occur within the Nafion tube since the presence of quenchers or dilution of the H_3PO_4 lead to shorter emission lifetimes. Intensity-time decay profiles from the transient emission experiments followed single exponential

kinetics for all of our determinations, indicating that uranyl is the only species contributing to the observed emission decay signal.

In addition to other emitting species, inorganic and organic quenchers are the major interferents which can hamper the accuracy of our analysis. Dissolved inorganic ions in solution have profound but varied effects on the excited state properties of UO_2^{2+} , generally quenching the emission.¹²⁻¹⁵ Anion quenchers such as Cl^- and Br^- should not diffuse very readily through the Nafion membrane of the sensor.^{10,11} To test the permselectivity of the Nafion, we analyzed solutions containing large excesses of KCl or KBr compared to 10^{-6} M UO_2 . As shown in Fig. 4, the sensor allows for uranyl analysis in the presence of a 1,000-fold molar excess of chloride without any decrease in signal intensity or excited-state lifetime. In marked contrast, pumping uranyl solutions containing chloride or bromide directly through the sensor, by-passing the Nafion diffusion step, drastically reduces both the emission intensity and lifetime (by $\sim 85\%$ for this case). In a separate experiment where the chloride concentration was held fixed at 2.7×10^{-4} M and the uranyl concentrations varied from 5×10^{-8} to 6×10^{-5} M, there was virtually no significant decrease in the uranyl excited state lifetime or emission intensity as the uranyl concentration decreases when the sensor is used. In the absence of the sensor, the uranyl lifetime decreases from ~ 200 μs to ~ 50 μs over the same concentration range and there is a corresponding decrease in emission intensity as well.

The major inorganic cation quenchers, which are Fe^{2+} , Pb^{2+} , and Ag^+ can pose significant problems since they can permeate the Nafion membrane.¹³⁻¹⁵ We are currently investigating the effects of these interferents and working on methods to eliminating this problem. One solution to this problem is to use the proprietary reagent Fluran, which effectively eliminates quenching due to Fe^{2+} and Pb^{2+} when they are at similar concentrations to the uranyl ion. The excited state lifetime of UO_2^{2+} in Fluran is ~ 55 μs . For a solution of 1×10^{-6} M UO_2 , this lifetime does not decrease with increasing iron or lead concentration until a molar excess of quencher compared to uranyl is reached.

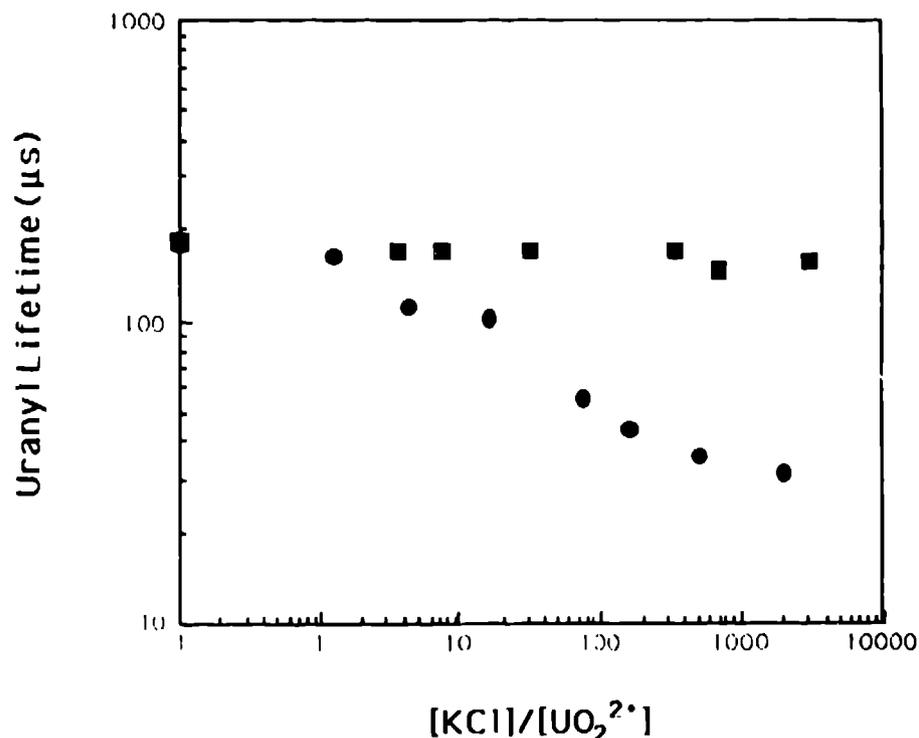


Figure 4. The uranyl excited-state decay rate constant is plotted as a function of the $\text{KCl}/\text{UO}_2^{2+}$ concentration ratio. (O), solutions pumped directly into the flow cell of the sensor; (□) solutions that had to pass through the Nafion membrane before entering the flow cell.

2.2 Response Characteristics of the Uranyl Sensor

To establish the response characteristics of the uranyl sensor, we determined the signal intensity between 45 and 55 μs after laser excitation at several concentrations of uranyl ion inside the flow chamber. A series of 0.75 M H_3PO_4 solutions of varying $[\text{UO}_2]^{2+}$ concentration pumped directly through the sensor, bypassing the Nafion diffusion step, gave results shown as the shaded circles in Fig. 4. Immersing the Nafion tube in deionized water solutions containing the same varying concentrations of $[\text{UO}_2]^{2+}$ for 30 min, allowing for diffusion, and then making the emission measurements gave the results shown as the triangles in Fig. 4. Those signals are approximately 10 times more intense than those obtained when the uranyl solutions were pumped directly through the flow optrode. Because phosphate is anionic and thus should not diffuse through the Nafion membrane and the uranyl ion forms a complex with phosphate ions, uranyl is concentrated from the sample into

the flow optrode. In addition, the phenomenon of Donnan dialysis may lead to a concentration enhancement.^{11,16} This concentration enhancement leads to a 10-fold increase in the detection limit ($\sim 5 \times 10^{-9}$ M rather than 5×10^{-8} M, based on a signal-to-noise ratio of 2). Figure 4 also shows two calibration curves obtained for uranyl nitrate/sodium nitrate solutions in which each data point was acquired after a 30-min equilibration time. These results indicate that the observed signals are independent of ionic strength.

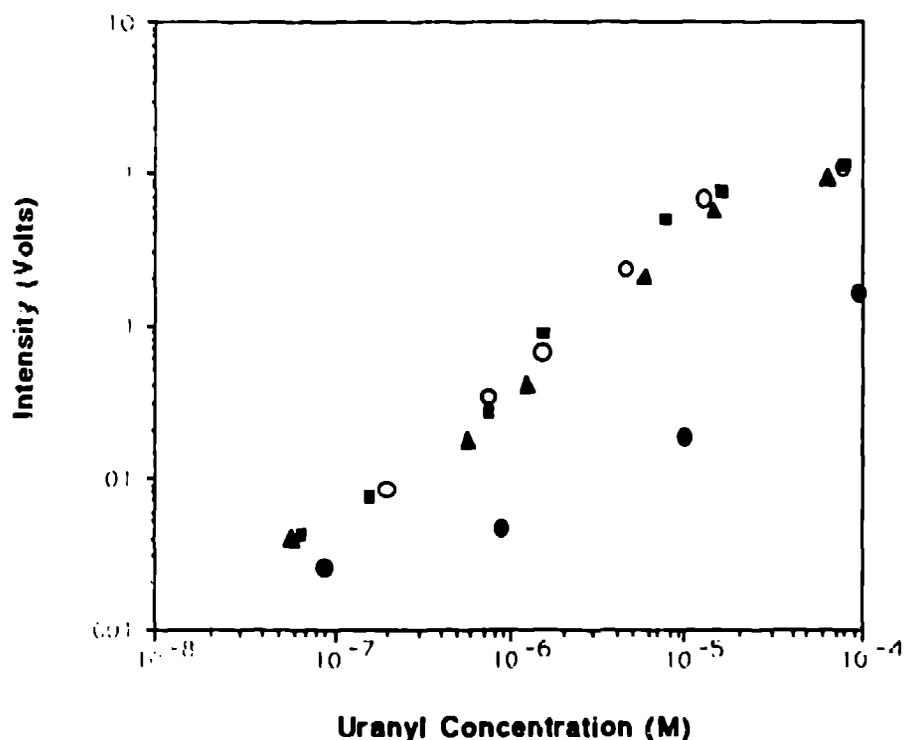


Figure 4. Plot of the average emission intensity between 45 and 55 μ s after excitation vs concentration for aqueous UO_2^{2+} over the range 5×10^{-8} M to 1×10^{-4} M using the uranyl sensor shown in Fig. 1 (O), $[\text{UO}_2]^{2+}$ pumped directly into the flow cell; (Δ), $[\text{UO}_2]^{2+}$ in a deionized water solution, $[\text{UO}_2]^{2+}$ in an aqueous solution of; (□), 1×10^{-2} M NaNO_3 ; (●), 1×10^{-4} M NaNO_3 . For the solutions that were not pumped directly into the flow cell, the uranyl ion was allowed to diffuse through the Nafion membrane into the flow cell over a period of 30 min.

In between uranyl determinations, the sensor was soaked in distilled water and the flow cell was flushed with several 50 μ l aliquots of 0.75 M

H₃PO₄. The reversibility of the system was shown by the fact that the intensity reading between uranyl determinations consistently returned to the baseline value, even after hundreds of experiments under differing conditions of uranyl, quencher, and electrolyte concentrations.

2.3 Osmotic Flow

Figure 5 shows the amount of osmotic flow that was observed using 1.5 M H₃PO₄ as the flow reagent and varying the cationic forms of the Nafion membrane. Nafion can be converted from one cationic form to another simply by equilibrating the membrane in a 0.1 M solution of the cation of interest for several hours. Since H₃PO₄ is present as well as an electrolyte solution, it is expected that only partial conversion from the H⁺ form will occur. Osmotic flow rates were determined by weighing the aqueous solution that drained out of the waste flow capillary tube on the uranyl sensor at five minute intervals and then converting these weights to volumes assuming a density of 1.0 g/ml. If it is assumed that the diffusion coefficient of water through the membrane remains constant, then the instantaneous flux is dictated by the difference in ionic strength across the membrane at a given time. The osmotic flow data in Figure 5 represents the total amount of water that passed through the membrane as a function of time. Initially, the relative difference in ionic strength across the Nafion membrane is great (1.5 M vs 10⁻⁵ M). As osmotic flow progresses, and the phosphoric acid solution on the inside of the Nafion tube is diluted, the total amount of water flowing across the membrane per unit time decreases. When the ionic strength of electrolyte is the same on both sides of the membrane, the net osmotic flow will stop.

This is a potentially damaging phenomenon from an analysis standpoint. Since the entire void volume of the Nafion tube is ~ 30 μl, osmotic flow can have pronounced dilution effects on the phosphoric acid solutions. When the phosphoric acid solution is diluted to ≤ 0.5 M, the uranyl emission intensity and excited state lifetime decreases dramatically. Between 0.5 and 2 M H₃PO₄ the UO₂ excited state lifetime varies only slightly as a function of phosphoric acid concentration. For example, dilution from 1.5 M to 0.75 M H₃PO₄ does not affect the analysis significantly.

Despite the presence of osmotic flow of water, we observe no decrease in excited state lifetime during our analysis. Even though dilution of the phosphoric acid certainly occurs as a consequence of osmotic flow, by pumping several 5 μl aliquots of phosphoric acid through the system to extract the uranyl from the membrane, the solution containing uranyl that reaches the analysis cell contains nearly the same concentration of H_3PO_4 that was originally in the system. The diluted H_3PO_4 is pushed through the flow cell and out of the system before the analysis is performed. This was evidenced by the fact that the lifetimes we observed during the experiments were consistent with using 1.5 M H_3PO_4 . ~ 200 μs . Dilution would lead to shorter lifetimes.

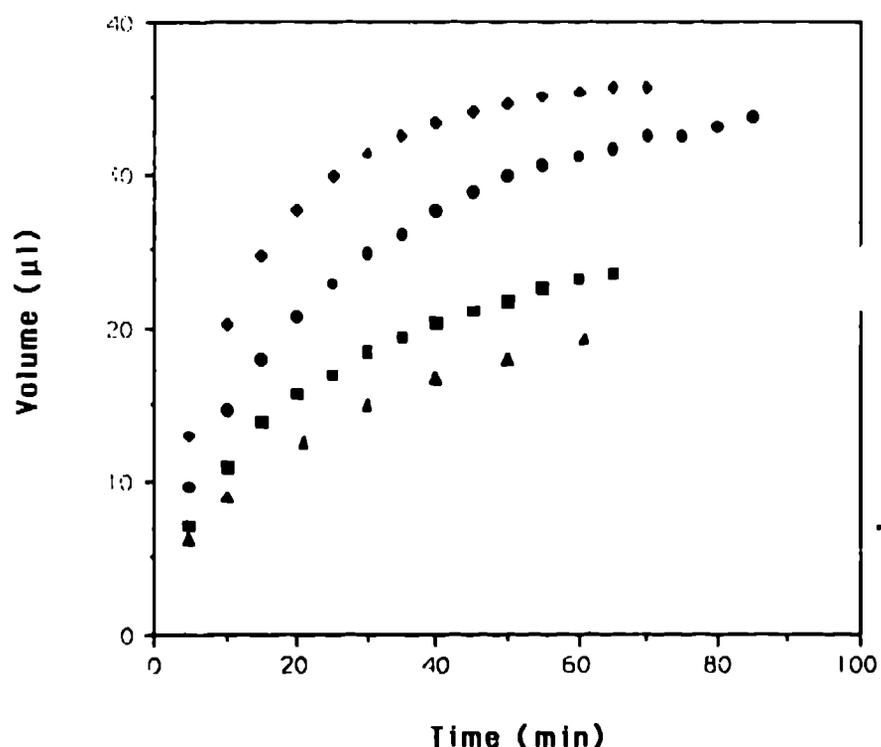


Figure 5. Osmotic flow as a function of time for the differing cationic forms of Nafion: (\diamond) H^+ , (\circ) Na^+ , (\square) Mg^{2+} , (\triangle) Ca^{2+}

Osmotic flow can be controlled to some extent by changing the counterion associated with the sulfate anion of the Nafion membrane. The diffusion coefficient of water through a Nafion membrane depends on the water content of the membrane.¹⁷ More hydrated films show larger diffusion coefficients than less hydrated films. The cationic form of the film, dictates, to a large extent, the degree of hydration of the film.¹⁷

The results depicted in Figure 5 confirm these observations. When the membrane is in the H^+ form (a highly hydrated form) we observe large osmotic flow rates. When the membrane is partially in the Na^+ form, we observe lower rates of osmotic flow. Although slower osmotic flow rates are desirable to lessen the effects of diluting the flow reagent, it is generally true that the transport rates of cations through Nafion membranes follow the same trends as water transport rates. Thus it is expected that for less-hydrated membranes, lower rates of uranyl transport may also be observed. We are presently investigating the interaction between uranyl transport rates and osmotic flow rates.

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